

SPECIFICATION

MATERIAL FOR NEGATIVE ELECTRODE OF LITHIUM SECONDARY  
BATTERY, METHOD FOR PRODUCTION THEREOF AND LITHIUM  
SECONDARY BATTERY USING THE SAME

5

TECHNICAL FIELD

The present invention relates to a carbon  
material and a method for production thereof, in  
particular, a carbon powder whose surface is coated with  
ingredients of heavy oil and a method for production  
10 thereof. Specifically, the invention relates to a carbon  
material, useful as material for negative electrode of  
lithium secondary battery, a method for production  
thereof and lithium secondary battery using such a carbon  
material.

15

BACKGROUND ART

Recently, miniaturization and weight-saving of  
electronic equipments, information related equipments and  
like portable-type equipments (hereinafter "portable  
equipment") have been progressed significantly, which  
20 makes secondary batteries driving said equipments very  
important parts. Lithium secondary batteries have  
lightness in weight and high energy density so that  
lithium secondary batteries are regarded as promising  
driving power source of portable equipment. Research and  
25 development thereof are actively progressed. When

lithium metal is used as negative electrode, dendrite formed and grown on metal lithium by repeating a charge and discharge cycle causes an internal short circuit, which makes production of lithium secondary battery  
5 difficult. Although use of lithium alloys, such as a lithium aluminium alloy in place of lithium metal is proposed, batteries using the alloy causes segregation of alloy in the course of charge and discharge cycle or deep charge and discharge. Consequently, batteries  
10 maintaining sufficient characteristics for a long period of time can not be obtained.

Batteries using carbon materials as host material of negative electrode to utilize an intercalation and deintercalation reaction of lithium ion  
15 are proposed, developed and come in practice. Lithium secondary batteries applying carbon materials to a negative electrode is superior in cycle characteristics, safety, etc.

Carbon materials have a variety of structures  
20 and forms from graphite to amorphous carbon. Performance of electrode is greatly influenced by physical properties and microstructure thereof formed by hexagonal net face of carbon. A variety of carbon materials whose physical properties and microstructure are specified are,  
25 therefore, proposed. Presently used materials for

negative electrode of lithium secondary battery are roughly classified into carbon-series materials calcined at about 1,000 °C and graphite-series materials calcined at about 2,800 °C. The former has an advantages of low  
5 reactivity with electrolyte leading to difficulty of electrolyte decomposition and a drawback of great change of electric potential with release of lithium ion. In contrast, the latter has an advantage of small change of electric potential with release of lithium ion and a  
10 drawback of reaction with electrolyte leading to decomposition of electrolyte and destruction of carbon materials (J. Electrochem. Soc. 117, 222 (1970)). As a result, the latter causes problems of decreased efficiency of charge and discharge, decreased cycle  
15 characteristics and decreased safety of battery. It is reported that graphite-series materials may be used, when specific electrolytes are used (J. Electrochem. Soc. 137, 2009(1990)). For the purpose of producing battery, however, limitation of electrolyte has a drawback of  
20 restraint of improvement of temperature characteristics and cycle characteristics of battery by the type of electrolyte.

To solve the problems, JP-A-4-368778, JP-A-4-370662, JP-A-5-94838 and JP-A-5-121066 proposed carbon  
25 materials produced by coating a surface of graphite

particles with low-crystalline carbon. These surface-modified carbon materials are effective to increase battery capacity and to improve cycle characteristics through inhibition of electrolyte decomposition.

5           According to techniques described in JP-A-4-368778, carbon coating layer formed in gas phase do not cause fusing and aggregation of carbon particles leading to generation of materials with high performance. However, the materials have practical problems in cost  
10   and mass production.

          JP-A-4-370662, JP-A-5-94838 and JP-A-5-121066 disclose a method of coating carbon in liquid phase which is advantageous in cost and mass production. However, a simple combination of mixing graphite particles and  
15   organic compounds in liquid phase with calcination thereof generates fused and aggregated carbon particles which are necessary to be powdered, causing drawbacks of exposure of generated active surface of graphite by powdering fused and aggregated carbon particles,  
20   contamination during powdering and complexity of production steps.

#### DISCLOSURE OF THE INVENTION

          It is a primary object of the invention to obtain a lithium secondary battery which is superior in  
25   properties such as cycle characteristics and safety by

manufacturing a negative electrode using carbon materials which are free of selectivity and/or restraint with respect to electrolytes, and small in change of electric potential with release of lithium ion.

5           The inventors conducted extensive research to solve or decrease said prior art problems and found that carbon materials whose core material is uniformly covered with pitch can be produced by dipping particle-like carbon materials to be core material (hereinafter  
10 referred to as "core carbon material" or "carbon material to be core material" or simply "core material") into raw material for coat-forming carbon material (for example, tar, pitch and like coal heavy oil or petroleum heavy oil; hereinafter may be referred to as simply "heavy oil  
15 etc."), followed by taking specific means to separate core material from heavy oil etc. It is found that the two-layered carbon material particles thus obtained have a spheric or ellipsoidal or similar shape, or a shape that edge parts of carbon crystal are rounded. As a  
20 result of measurement by a BET method, it is found that specific surface area of the particles are smaller than core carbon materials before treatment showing that pores concerning specific surface area determined by a BET method are filled in a certain way.

25           According to the invention, coated carbon

material particles characterized in that carbon materials derived from heavy oil etc. are partially or entirely adhered to edge and basal plane of carbon materials to be core material, or, part or whole of the edge and basal  
5 plane are coated by the carbon material to be substantially spheric or ellipsoidal shape are provided. With respect to the carbon materials, pores concerning specific surface area determined by a BET method are filled by adhesion or coating of carbon derived from  
10 heavy oil etc. thereto, and the carbon materials have a specific surface area of  $5\text{m}^2/\text{g}$  or less (preferably about  $1\text{-}5\text{m}^2/\text{g}$ ).

According to the invention, carbon materials to be core material are highly crystalline graphite material  
15 having a mean interplanar spacing ( $d_{002}$ ) of (002) plane of 0.335-0.340 nm, a thickness of crystallite size in direction of (002) plane ( $L_c$ ) of at least 10 nm (preferably at least 40 nm), a thickness of crystallite size in direction of (110) plane ( $L_a$ ) of at least 10 nm  
20 (preferably at least 50 nm) determined by X-ray wide-angle diffractometry.

The carbon material of the invention is characterised by lower crystallinity of carbon materials adhered to or coated on the surface of core material  
25 (hereinafter may be referred to as "carbon material for

coating formation") than crystallinity of said core material.

The carbon material of the invention has a true specific gravity of 1.50 to 2.26g/cm<sup>3</sup>.

5           A lithium secondary battery with high capacity and safety may be obtained by using such carbon material as material of negative electrode of lithium secondary battery.

          Said coated carbon material of the invention  
10   may be produced as follows. The carbon material to be core material is dipped into tar, pitch and like coal heavy oil or petroleum heavy oil, preferably at about 10-300 °C for coating with heavy oil etc., followed by separating the coated core carbon material from heavy  
15   oil, adding an organic solvent to the coated carbon material thus separated for washing preferably at about 10-300 °C, and then drying the material.

          Furthermore, the invention provides a method for producing a carbon material comprising calcining for  
20   carbonization the carbon material coated with heavy oil etc. obtained according to the above-mentioned procedure and a method for producing a carbon material comprising calcining for graphitization the carbon material coated by heavy oil etc. obtained according to the above-  
25   mentioned procedure.

With respect to the invention, the carbon material obtained according to said manufacturing method comprises preferably 10% or less of particles having a diameter of 1  $\mu\text{m}$  or less as volume-based integrated value, wherein said diameter is determined by laser diffraction-type particle size distribution.

According to the invention, tar or pitch modified by removing at least part of primary QI to reduce a remaining primary QI of 3% or less (preferably 1% or less) is preferable.

Furthermore, the invention provides a material for negative electrode of lithium secondary battery characterized in that the material comprises said carbonized or graphitized carbon materials; a negative electrode for lithium secondary battery using the material for negative electrode; and also a non-aqueous lithium secondary battery and a solid electrolyte secondary battery using the negative electrode.

With respect to the invention, "nearly spheric or ellipsoidal" carbon materials include carbon materials free of sharp edge by adhesion of carbon ingredients from heavy oil etc. to edge and basal plane of carbon material to be core material partially or entirely, and shapes of carbon material particles to be core material observed by SEM are maintained. The carbon material may be



efficiently produced by the method of the invention free of grinding step. However, the material is not limited to the material produced by the method of the invention.

With respect to the invention, carbon materials  
5 whose "pores concerning specific surface area determined by a BET method are coated and filled by raw material for coat-forming carbon material, i.e., carbon materials from tar, pitch and like coal heavy oil or petroleum heavy oil adhered thereon" include carbon materials whose pores  
10 concerning specific surface area determined by a BET method is filled at least part thereof by calcined product of raw material for coat-forming carbon material (hereinafter referred to as coat-forming carbon material). Specifically, it is not necessary for the  
15 pores to be completely filled by carbon materials derived from heavy oil etc. For example, carbon materials whose adjacent entry ports are filled are included. Such conditions of carbon materials may be confirmed by reduction of specific surface area determined by a BET  
20 method .

The carbon materials obtained according to the invention include 4 combinations, i.e., low-crystallinity carbon material + low-crystallinity carbon material; low-crystallinity carbon material + high-crystallinity carbon  
25 material; high-crystallinity carbon material + low-

crystallinity carbon material; and high-crystallinity carbon material + high-crystallinity carbon material. In all cases, an effect on decrease of electrolyte degradation is exerted.

5               With respect to the invention, low-crystallinity carbon materials means "carbon which may not be graphite crystals by a treatment necessary for graphitization (eg. treatment at elevated temperature)". Such carbon is usually referred to as hard carbon. On  
10   the other hand, high-crystallinity carbon material means "carbon which becomes graphite crystals by a treatment for graphitization". Such carbon is usually referred to as soft carbon.

              According to the invention, the following 8  
15   carbon materials are obtained depending on a combination of core material and outer carbon material (which may be referred to as "coat-forming carbon material", "carbon material for surface-modification", "covering material") and on final calcination temperature. Examples are:

20   (1) carbonized carbon materials comprising core material consisting of low-crystallinity carbon materials and coat-forming carbon materials consisting of low-crystallinity carbon materials;

              (2) carbonized carbon materials comprising core material  
25   consisting of low-crystallinity carbon materials and

coat-forming carbon materials consisting of high-crystallinity carbon materials;

(3) graphitized carbon materials comprising core material consisting of low-crystallinity carbon materials and

5 coat-forming carbon materials consisting of low-crystallinity carbon materials;

(4) graphitized carbon materials comprising core material consisting of low-crystallinity carbon materials and coat-forming carbon materials consisting of high-

10 crystallinity carbon materials;

(5) carbonized carbon materials comprising core material consisting of high-crystallinity carbon materials and coat-forming carbon materials consisting of low-crystallinity carbon materials;

15 (6) carbonized carbon materials comprising core material consisting of high-crystallinity carbon materials and coat-forming carbon material consisting of high-crystallinity carbon materials;

(7) graphitized carbon materials comprising core material  
20 consisting of high-crystallinity carbon materials and coat-forming carbon material consisting of low-crystallinity carbon materials;

(8) graphitized carbon materials comprising core material consisting of high-crystallinity carbon materials and  
25 coat-forming carbon material consisting of high-

crystallinity carbon materials.

According to the invention, carbon materials for secondary batteries having small specific surface area and good charge and discharge properties may be efficiently produced by coating core material with outer carbon materials. In particular, carbon materials for battery with excellent charge and discharge properties may be obtained by a combination of core material and covering material shown in (5), (6) and (7), and also carbon materials for battery with small specific surface area and improved safety may be obtained by a combination of core material and covering material shown in (1), (2), (3), (4) and (8).

According to the invention, as carbon material to be core material, one or more of particle-like (scaly or massive, fibrous, whisker-like, spheric, shattered etc.) natural graphite, artificial graphite, mesocarbon microbeads, mesophase pitch powder, isotropic pitch powder, resin and carbonized and graphitized products thereof. In particular, scaly and massive natural graphite and artificial graphite which are very inexpensive are preferable from the viewpoint of cost. The carbonized and graphitized products of mesocarbon microbeads (MCMB) having very small specific surface area leading to obtaining material having smaller specific

surface area are preferable from the viewpoint of safety of secondary battery, if the products are used as core material.

Carbon materials to be core material are more preferably, 0.335-0.340 nm in mean interplanar spacing (d002) of (002) plane, at least 10nm (preferably at least 40 nm) in thickness of crystallite size in direction of (002) plane (Lc), at least 10 nm (preferably at least 50 nm) in thickness of crystallite size in direction of (110) plane (La) determined by X-ray wide-angle diffractometry, and 0.5 or less (preferably 0.4 or less) in ratio of peak strength around  $1360\text{cm}^{-1}$  to peak strength around  $1580\text{cm}^{-1}$  (hereinafter referred to as R value) determined by Raman spectroscopy with argon laser.

When the mean interplanar spacing is more than 0.340 nm, or Lc and La are smaller than 10nm, or R value is more than 0.5, crystallinity of carbon materials is insufficient, and covering carbon materials produced therefrom are not preferable because of insufficient capacity at low electric potential near dissolution and deposition of lithium (0-300mV on the potential vs.  $\text{Li/Li}^+$ ).

Particle size distribution of carbon materials to be core material is preferably about 0.1-150  $\mu\text{m}$ .

Since particle size of final product containing coat-

forming carbon material derived from heavy oil etc.  
substantially depends on particle size of carbon material  
to be core material, particle size of the final product  
is substantially specified by particle size of core  
5 material. When particle size of core material is less  
than 0.1  $\mu\text{m}$ , internal short circuit is likely to be  
caused through pores of separator of battery, thereby not  
preferable. On the other hand, when particle size of  
core material is more than 150  $\mu\text{m}$ , uniformity of  
10 electrode, packing density of active material and  
handling properties during steps of production of  
electrode are decreased, thereby not preferable.

A weight ratio of coat-forming carbon material  
derived from heavy oil etc., that is, coat-forming carbon  
15 material/(core carbon material + coat-forming carbon  
material) (hereinafter the ratio is referred to as  
"covering ratio") is preferably more than 0 and up to  
0.3, more preferably 0.01-0.2. In this case, thickness  
of coat-forming carbon is about 0.01-10  $\mu\text{m}$ , more  
20 preferable thickness is about 0.05-5  $\mu\text{m}$ .

When a covering ratio exceeds 0.3, to ensure  
sufficient capacity of battery produced therefrom becomes  
difficult. The amount of coat-forming carbon is  
determined as quinoline soluble matter by solvent  
25 analysis of carbon components from heavy oil etc. which

cover surface of core material before calcination.

Thickness of coat-forming carbon materials is determined by measuring a central particle size (D50) of carbon material to be core material before coating and a central  
5 particle size (D50) of pitch-coated carbon materials before calcination with a laser diffraction particle size analyzer, followed by calculating the thickness using the equation :  $\{(\text{particle size after coating}) - (\text{particle size of raw material before coating})\} / 2$  based on the  
10 assumption that carbon materials are spheric and that shape of coat layer comprising pitch components is maintained after calcination.

According to the invention, a combination that a coat-forming carbon material on the surface has lower  
15 crystallinity than a core carbon material is preferable. Furthermore, a mean interplanar spacing (d002) of (002) plane of 0.335-0.340 nm, a thickness of crystallite size in direction of (002) plane (Lc) of at least 10 nm (preferably at least 40 nm) and a thickness of  
20 crystallite size in direction of (110) plane (La) of at least 10 nm (preferably at least 50 nm) determined by X-ray wide-angle diffractometry, and 0.5 or more (preferably about 0.5-1.5) determined by Raman spectroscopy with argon laser are preferable. The  
25 interplanar spacing and R value are general index of

crystallinity of graphite. From the nature of the measuring methods, X-ray diffractometry reflects bulk properties on determined value of physical property, on the other hand, Raman spectrometry reflects physical properties of surface of material. Specifically, materials which meet said physical properties mean that the materials have high crystallinity as bulk property and low crystallinity as surface thereof. When R value of material after calcination is less than 0.5, selectivity of solvent thereof is not completely removed because of high surface crystallinity. When mean interplanar spacing (d002) is outside of the range of 0.335-0.340 nm, change of electric potential with intercalation and deintercalation of lithium ion become large, thereby not preferable.

A true density of the coated carbon materials with two-layer structure obtained is about 1.50-2.26g/cm<sup>3</sup>, preferably about 1.8-2.26g/cm<sup>3</sup>, more preferably about 2.0-2.26g/cm<sup>3</sup>. When electrode is produced using material with low true density, obtaining battery with high capacity is difficult, since increase of density of active substance in electrode is not possible even if the material has superior properties per unit weight.

Coated carbon materials preferable have a



particle size distribution ranging from 0.1 to 150  $\mu\text{m}$ .

Within the range of particle size distribution, the material preferably has 10% or less of particles having a diameter of 1  $\mu\text{m}$  or less based on volume thereof. When  
5 content of particles with a diameter of 1  $\mu\text{m}$  is more than 10% based on volume thereof, battery properties are decreased due to increase of specific surface area, thereby not preferable.

The coated carbon materials in powder form  
10 obtained according to the invention may be subjected to mold fill-out, pressure molding and calcination to obtain a carbon block or a graphite block with homogenous composition.

Examples of raw material of coat-forming carbon  
15 material are naphthalene, phenanthrene, acenaphthylene, anthracene, triphenylene, pyrene, chrysene, perylene and like aromatic hydrocarbons, tar or pitch obtained by polycondensation thereof under pressure with heat, or, tar, pitch, asphalt and oils containing a mixture of said  
20 aromatic hydrocarbons as main component which may be derived from petroleum oil and coal oil. In the specification, the raw material of coat-forming carbon material may be simply referred to as "(petroleum or coal) heavy oil, etc.". Furthermore, a variety of  
25 thermoset resins may be used as coat-forming raw

material, although they are disadvantageous in cost.

When coal heavy oil is used, tar or pitch having 3% or less (preferably 1% or less) of primary QI produced by removing at least part of primary QI which exists in raw material is preferably used. The primary QI means free carbon essentially included in coal tar. The primary QI which exists in raw material inhibits carbonization by calcination and is contaminated in the final product as spheric carbon particles having a diameter of about 1  $\mu\text{m}$ , which may result in introduction of problems in manufacturing process of electrode or decrease of electrode properties.

In general, heavy oil is solid at ordinary room temperature and may be softened and melted by heating. The temperature at which material become softening is referred to as softening point (SP). In order to specify quality of heavy oil, insoluble matter in toluene determined by solvent fractionation with toluene is usually used. Those are typical indications to specify heavy oil. According to the invention, optional indication may be suitably selected to specify quality of heavy oil.

According to the invention, carbon materials to be core material is mixed with heavy oil etc. and stirred. Stirring methods are not specifically limited

to, but include mechanically stirring methods using ribbon mixer, screw-type kneader, universal mixer and the like.

Conditions for stirring treatment (temperature and time) are suitably selected in compliance with components of raw material (core material and coat-forming heavy oil) and viscosity of mixture. The conditions are usually about 10-300°C, more preferably about 50-200°C. Time period may be determined to make viscosity of mixture of 5000 Pa·s or less. The thickness of coating layer of coat-forming raw material (which hereinafter may be referred to as simply coating layer) may be controlled by adjusting temperature and time period during a stirring treatment. Higher temperature and/or shorter time lead to a thinner coating layer. In contrast, lower temperature lead to a thicker coating layer. Insufficient stirring causes ununiform coating layer, thereby not preferable. In general, stirring time does not adversely affect properties of product. However, too long stirring time practically decreases productivity, thereby not preferable. Time period may be suitably selected.

Atmosphere during stirring may be under any of atmospheric pressure, application of pressure and reduced pressure. Stirring under reduced pressure improves

conformability of core material with heavy oil, thereby preferable.

According to the invention, a plural of mixing and stirring processes may be conducted for the purpose of increased conformability of core material with heavy oil, uniform thickness of coating layer and thicker coating, if necessary. Before the following washing step, the coated core material may be separated and then subjected to washing step.

Subsequently, the carbon materials coated by heavy oil etc. thus obtained is subjected to a washing step. Examples of organic solvent used for washing are toluene, quinoline, acetone, hexane, benzene, xylene, methylnaphthalene, alcohols, solvents from coal oil and petroleum oil. Among them, toluene, quinoline, acetone, benzene, xylene, methanol, gas oil and middle oil from coal and petroleum are more preferable. Heavy oil components in coating layer may be controlled by imparting insoluble matters in washing solvent to coating layer, if organic solvents are suitably selected.

Washing temperature is determined according to finally obtainable coated carbon materials, in particular, properties of surface of coating layer. The temperature is not specifically limited, but is preferably about 10-300 °C.

A proportion of solid matter { = core material + coating layer or impregnation layer (hereinafter simply referred to as coating layer)} and organic solvent during washing is preferably 1 : 0.1-10 by weight ratio.

5           In the washing step, thickness and remaining heavy oil components of coating layer may be controlled by selecting the type of solvent, washing time and washing temperature. For example, coating layer become thin by a suitable combination of solvent with high  
10           detergency and elevating washing temperature. On the other hand, thickness of coating layer become thick by a suitable combination of solvent with low detergency and decrease of washing temperature. Washing time are selected according to said conditions.

15           Subsequently, separation step of coated carbon materials from organic solvent may be conducted according to centrifugation, press filtration, gravity settling and like techniques. Temperature during separation is usually about 10-300°C.

20           Drying of separated coated carbon materials is usually conducted about 100-400°C.

          The dried coated carbon materials maintain pitch components on the surface of core material particles leading to no fusing and aggregation of  
25           particles.

Said coated carbon materials thus dried are then calcined. For carbonization of coated carbon materials, calcination may be carried out at temperature of about 600-2,000°C, preferably 900-1,300°C. For  
5 graphitization, calcination may be carried out at temperature of about 2,000-3,000°C, preferably about 2,500-3,000°C.

In order to maintain low crystallinity during calcination at elevated temperature in conditions of  
10 carbonization or graphitization, coated heavy oil layer may be subjected to a graphitization retardation treatment using oxidative gases such as oxygen, ozone, carbon monoxide and sulfur oxide before calcination of coated carbon materials, followed by calcined at elevated  
15 temperature. For example, highly crystallizable coating layer is formed on highly crystallizable core material, and then oxidation treatment is conducted to convert a coating layer into lower crystallizable carbon. In contrast, highly crystallizable coating layer may be  
20 maintained without said oxidation treatment. Such oxidation treatment is conducted before calcination of coated carbon materials. The carbon materials thus obtained is useful as material for negative electrode of lithium secondary battery.

25 Examples of atmosphere during calcination of

coated carbon materials are reducing atmosphere, inert gas flow, inert gas in closed system, vacuum condition and like non-oxidative atmosphere.

Irrespective of calcination temperature, a rate of elevation of temperature is selected from about 1-300°C/hr. Calcination time is about 6 hours to 1 month. Elevation of temperature may be conducted step-by-step in compliance with thickness of coating layer.

Vacuum calcination is preferably carried out with maintaining reduced pressure at a temperature from normal temperature to the highest temperature, or, at a suitable temperature range (preferably more than 500°C). Vacuum calcination is effective to remove surface functional groups of coated carbon materials leading to reduction of non-reversible capacity of battery.

In general, a rapid rate of elevating temperature is expected to improve productivity, and a slow rate of elevating temperature (up to 10°C/hr) is expected to form a densified coating layer. Temperature profile during elevation of temperature and calcination may be in a variety of manners such as linear elevation of temperature and stepwise elevation of temperature by holding temperature for a constant period of time.

When the carbon materials thus obtained whose surface is coated by coat-forming carbon materials are

applied to negative electrode of lithium secondary battery, decomposition of electrolyte and destruction of carbon materials are inhibited due to low reactivity thereof with organic solvent of electrolyte solution. As  
5 a result, the battery has advantages of improved charge and discharge efficiency and safety. In general, graphite material has an outside-oriented active edge plane of crystal lattice so that graphite material is likely to react with electrolyte. According to the  
10 invention, since the active edge plane of crystal lattice is covered by pitch components whose basal plane, i.e., condensed polycyclic network of carbon, orientates outside, reaction with organic solvent of electrolyte will be inhibited.

15 According to the invention, since the amount of coating heavy oil on the surface of carbon materials and thickness of coating layer may be controlled by adjusting temperature and time of dipping carbon materials to be core material into heavy oil etc., or, the type of  
20 organic solvent and washing conditions (time and temperature) for washing coated carbon materials, carbon materials whose surface is covered by pitch components may be produced, wherein said pitch components have basal plane, i.e., condensed polycyclic network of carbon,  
25 which orientates in a direction of surface of carbon



materials.

Furthermore, with respect to the coating of core material surface, orientation of the basal plane in the direction of surface of carbon material is maintained during carbonization or following graphitization of these carbon materials. When the carbon material is applied to negative electrode of lithium secondary battery, since the carbon materials is unlikely to react with organic solvent, decomposition of electrolyte and destruction of carbon materials will not occur. Consequently, superior effects, such as high charge and discharge efficiency of battery and good safety of battery, are exerted.

In order to produce a lithium secondary battery of the invention, particle size of the coated carbon materials thus obtained is optionally adjusted by treatments such as dispersion and classification to be material for electrode.

Electrode is produced by mixing the carbon materials with binders and like known materials, followed by forming active material layer on collector. Binders are not specifically limited. Examples of binders are polytetrafluoroethylene, poly(vinylidene fluoride), and like fluorine-containing polymer; polyethylene, polypropylene, and like polyolefins; synthetic rubbers. The amount of binders are usually about 3-50 parts by

weight, preferably about 5-20 parts by weight, more preferably about 5-15 parts by weight based on 100 parts by weight of active material. An excessive amount of binder decreases a density of active material, thereby not preferable. A too small amount of binder has an insufficient ability to retain active material in electrode resulting in low stability of electrode, thereby not preferable. Examples of methods for producing an electrode are a method comprising producing paste by mixing active material and a binder, and forming an active material layer on collector with doctor blade or bar coater; and a method comprising adding a mixture of an active material and a binder to a press machine and forming a shaped form by pressing.

Known organic electrolyte solutions, inorganic solid electrolytes, solid polymer electrolytes may be used as electrolyte of lithium secondary battery of the invention.

The organic electrolyte solutions are in particular preferable from the viewpoint of ion conductivity. Examples of solvents for organic electrolyte solutions are propylene carbonate, ethylene carbonate, butylene carbonate, diethyl carbonate, dimethyl carbonate, methylethyl carbonate,  $\gamma$ -butyrolactone, and like esters; tetrahydrofuran, 2-

methyln-tetrahydrofuran and like substituted tetrahydrofuran; dioxolane, diethylether, dimethoxyethane, diethoxyethane, methoxyethoxyethane and like ethers; dimethylsulfoxide, sulfolane, methylsulfolane, acetonitrile, methyl formate and methyl acetate, which may be used singly or a mixture thereof. Examples of electrolytes are lithium perchlorate, lithium borofluoride, lithium hexafluorophosphate, lithium hexafluoroarsenate, sodium trifluoromethanesulfonate, lithium halide, lithium chloroalminate and like lithium salts, which are used singly or in a mixture thereof. Organic electrolyte solutions are prepared by dissolving electrolytes in said solvents. Solvents and electrolytes to prepare electrolyte solution is in no way limited to said examples.

Examples of inorganic solid electrolytes are nitride, halide, oxygen acid salts and phosphorous sulfide compounds of lithium, specifically,  $\text{Li}_3\text{N}$ ,  $\text{LiI}$ ,  $\text{Li}_3\text{N-LiI-LiOH}$ ,  $\text{LiSiO}_4$ ,  $\text{LiSiO}_4\text{-LiI-LiOH}$ ,  $\text{Li}_3\text{PO}_4\text{-Li}_4\text{SiO}_4$  and  $\text{Li}_2\text{SiS}_3$ .

Examples of organic solid electrolytes are substances comprising said electrolytes and dissociative polymers, and polymers with ion dissociative group or groups. The dissociative polymers include polyethyleneoxide derivatives and polymers including the

derivatives, polypropyleneoxide derivatives and polymers including the derivatives, poly(phosphate ester).

Polymer matrix material including said aprotic polar solvents, a mixture of polymer with ion dissociative

5 group or groups and aprotic polar solvent, material prepared by adding polyacrylonitrile to electrolyte may be used. Inorganic solid electrolyte and organic solid electrolyte may be used in combination.

Positive electrode of lithium secondary battery  
10 of the invention may be prepared according to conventional manner using lithium-containing oxide as active material of positive electrode. Examples of active material of positive electrode are  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiFeO}_2$ ,  $\text{LiMnO}_2$ , and analogs of the compounds  $\text{Li}_x\text{M}_y\text{N}_z\text{O}_2$   
15 wherein M represents any of Fe, Co, Ni and Mn, N represents a transition metal, 4B group metal or 5B group metal),  $\text{LiVO}_2$ , which are mixed with electrically-conductive materials, binders and optionally with solid electrolytes to form a positive electrode. A mixing  
20 ratio of the materials is about 5-50 parts by weight of electrically-conductive materials, about 1-30 parts by weight of binder based on 100 parts by weight of active material. Such electrically-conductive materials are not specifically limited to, but include known carbon black  
25 (acetylene black, thermal black, channel black etc.) and

like carbons, graphite powder and metal powder. Binders are not specifically limited to, but include known polytetrafluoroethylene, poly(vinylidene fluoride), and like fluorine-containing polymers; polyethylene, 5 polypropylene, and like polyolefins; and synthetic rubbers. In case that loadings of electrically-conductive material are less than 5 parts by weight or that loadings of binder are more than 30 parts by weight, practical lithium secondary battery can not be produced 10 due to increased resistance or polarization of electrode and decreased discharge capacity. More than 50 parts by weight (relative ratio thereof is varied according to the type of electrically-conductive materials) of electrically-conductive material result in decreased 15 amount of active material included in electrode leading to decreased discharge capacity of positive electrode. Less than 1 part by weight of binder results in insufficient integrity. More than 30 parts by weight of binder cause a decreased amount of active material 20 included in electrode, an increased resistance or polarization of electrode and a decreased discharge capacity similar to electrically-conductive materials, thereby not practical. Production of positive electrode is conducted preferably by heat treatment near melting 25 point of binder to improve integrity thereof.

Examples of separator to retain electrolyte solutions are known woven or unwoven fabric of electrical insulators such as synthetic resin fiber, glass fiber and natural fiber, powder molding of alumina and the like.

5 In particular, unwoven fabric of synthetic resin such as polyethylene and polypropylene are preferable from the viewpoint of stability of quality. An unwoven fabric of synthetic resin which is endowed with blocking function between positive and negative electrodes exerted by  
10 melting the separator with abnormal exothermic heat of battery is suitably used from the viewpoint of safety. A thickness of separator is not specifically limited, as long as separator may retain a required amount of electrolyte solution and inhibit short circuit between  
15 positive and negative electrodes, but generally about 0.01-1 mm, preferably about 0.02-0.05mm.

Materials of collector are not specifically limited to, but include known metals such as copper, nickel, stainless steel, aluminum and titanium in a form  
20 of metallic foil, mesh, porous body and so on.

#### Effect of the Invention

According to the invention, novel carbon materials, in which surface of carbon materials to be core material is coated with heavy oil etc., may be  
25 obtained by dipping carbon materials, in particular,

high-crystallinity graphite-type materials into tar, pitch and like coal heavy oil or petroleum heavy oil, followed by separating coated carbon materials from heavy oil etc., washing with organic solvent and drying.

5           The carbon materials with a specific structure, wherein the surface of core material comprising graphite-type material with high crystallinity is covered by carbon-type material with low crystallinity, may be obtained by carbonization of graphite-type material whose  
10 surface is uniformly coated with pitch at 600-2,000°C.

          According to the method for production of the invention, since no fusing or aggregation between particles occurs, when core carbon materials coated with pitch, tar and like heavy oil is washed, dried and  
15 calcined, no grinding is required leading to preparation of near spheric, so called "edgeless", particles. The particles are free of deterioration factor, i.e., contamination during grinding.

          When non-aqueous secondary batteries or solid  
20 electrolyte batteries are prepared using the coated carbon materials of the invention, in particular carbon materials prepared by coating surface of graphite material with heavy oil etc. or calcination product thereof, the batteries are superior in both charge and  
25 discharge properties and safety.

The production method of the invention using inexpensive natural and artificial graphites and the like as core material, and inexpensive pitch, tar and the like as coating material is a simple and highly productive  
5 method so that inexpensive and high performance material for negative electrode of lithium secondary battery may be obtained.

Furthermore, according to the invention,  
possible are 4 combinations between core materials and  
10 surface materials including low-crystallinity carbon material + low-crystallinity carbon material; low-crystallinity carbon material + high-crystallinity carbon material; high-crystallinity carbon material and low-crystallinity carbon material; and high-crystallinity  
15 carbon material and high-crystallinity carbon material. Eight type of carbon materials are obtained in further consideration of 2 calcination step (carbonization step and graphitization step). Carbon materials comprising combinations of carbonization-treated high-crystallinity  
20 carbon material + low-crystallinity carbon material and high-crystallinity carbon material + high-crystallinity carbon material; and also graphitization-treated high-crystallinity carbon material + low-crystallinity carbon material are, in particular, useful as materials for  
25 negative electrode of lithium secondary battery because



of low reactivity with electrolyte and remarkable charge and discharge properties.

Best Mode for Carrying out the Invention

The inventions are described below in detail.

- 5 A variety of determinations are carried out according to the following ways.

1. Determination of particle diameter

Center particle diameter and particle size distribution of particles are determined with "FRA9220  
10 Microtrac" product of Nikkiso.

2. Determination of covering ratio and coating thickness

With respect to carbon components from heavy oil covering the surface of core material before calcination, quinoline insoluble matter (%) was  
15 determined by an analysis with solvent according to the method specified by JIS K2425 so as to calculate quinoline soluble matter (%) was calculated according to "100 - (quinoline insoluble matter)". The amount of quinoline soluble matter corresponds to the amount of  
20 coat-forming carbon material.

A weight ratio of carbon materials for coating formation/(core carbon materials + carbon materials for coating formation) was calculated according to above-mentioned method.

25 3. Determination of specific surface area

The specific surface area was determined with "ASAP2400/nitrogen adsorption BET specific surface area measuring equipment" product of Micromeritics.

4. Determination of true specific gravity

5 True specific gravity was determined according to the method specified by JIS R7212.

5. Determination of crystal lattice size according to X-ray wide-angle diffractometry

Determination of crystal lattice size ( $L_c$ ,  $L_a$ ) according to X-ray wide-angle diffractometry was conducted by a known method described in "CARBON MATERIAL EXPERIMENTAL TECHNIQUE 1, pp.55-63, Ed. Carbon Material Society (KAGAKUGIJYUTUSYA)". For the shape factor  $K$ , 0.90 was used.

15 6. Raman spectrometric analysis

Furthermore, as surface physical properties of carbon materials,  $R$  value was determined as ratio of peak strength of  $1360\text{cm}^{-1}/1580\text{cm}^{-1}$  using 2 peaks observed by Raman spectrometric analysis with an argon laser at 20 514.5nm.

7. Determination of generated gas by immersing a negative electrode in electrolyte solution, followed by maintaining at elevated temperature

A pitch-coated carbon material (pitch-coated 25 graphite) was calcined at  $2,800^\circ\text{C}$  for 1 hour under

nitrogen atmosphere for graphitization. 95 parts by weight of graphitized pitch-coated graphite and 5 parts by weight of dispersion-type PTFE ("D-1" product of Daikin Industries Ltd.) were mixed, uniformly stirred in liquid phase and dried to make a paste-like material. 0.25g of the material for negative electrode was molded by a pressing machine to produce a negative electrode body having a diameter of 2cm, and then dried in vacuo at 200°C for 6 hours.

Subsequently, the negative electrode was charged until electric potential thereof in electrolyte became 0 V. The charged negative electrode was placed into a beaker cell with 25 ml of electrolytic solution, which was heated at 60°C for 6 hours to determine the amount of generated gas per 1g of graphitized pitch-coated graphite.

As electrolytic solution, a mixed solvent of ethylene carbonate, diethyl carbonate and methyl propionate (3:3:4 ratio by volume) in which 1 mol $\text{dm}^{-3}$  of  $\text{LiClO}_4$  was dissolved was used.

8. Production of non-aqueous battery and determination of battery properties

A positive electrode is generally prepared by mixing material for positive electrode, electrically-conductive material and binder. Carbon black, graphite

and like carbon materials or metal powder, metal-wool,  
and like metallic substances are suitably used as  
electrically-conductive materials. Binders may be mixed  
in the form of powder, or in the form of dispersion or  
5 dissolved solution so as to improve integrity. When such  
a dispersion or dissolved solution thereof is used,  
removal of the solvent by vacuum treatment, heat  
treatment or like means is required. Integrity may be  
further improved by heat-treatment at near melting point  
10 depending on the type of binders.

In examples of the present application, a  
mixture of 100 parts by weight of  $\text{LiCoO}_2$  as material for  
positive electrode, 10 parts by weight of acetylene black  
as electrically-conductive material and 10 parts by  
15 weight of PTFE powder as binder was formed into electrode  
having a diameter of 10mm to obtain a positive electrode  
body.

A negative electrode body is produced as  
follows in examples of the present application.

20 Pitch-coated graphite was calcined at  $1,000^\circ\text{C}$   
for 1 hour for carbonization. 95 parts by weight of the  
carbonized pitch-coated graphite and 5 parts by weight of  
dispersion-type PTFE ("D-1" product of Daikin Industries  
Ltd.) were mixed, uniformly stirred in liquid phase and  
25 dried to make paste-like material. 30mg of the material

for negative electrode was molded by a pressing machine to produce a negative electrode body having a diameter of 10mm, and then dried in vacuo at 200°C for 6 hours.

5 Separately, pitch-coated graphite was calcined at 2,800°C for 1 hour for graphitization. 95 parts by weight of the graphitized pitch-coated graphite and 5 parts by weight of dispersion-type PTFE ("D-1" product of Daikin Industries Ltd.) were mixed, uniformly stirred in liquid phase and dried to make paste-like material. 30mg  
10 of the material for negative electrode was molded by a pressing machine to produce a negative electrode body having a diameter of 10mm, and then dried in vacuo at 200°C for 6 hours.

Polypropylene unwoven fabric was used as  
15 separator.

Electrical discharge properties of coin-type lithium secondary battery, prepared by using the positive electrode body, the negative electrode body, the separator and the electrolytic solution thus  
20 obtained, were determined. The determination was carried out under constant-current charge and discharge of 1mA/cm<sup>2</sup>. Discharge capacity was regarded as capacity until battery voltage was decreased to 1.2V.

9. Preparation of solid electrolyte battery and  
25 determination of battery properties

The paste-like material of negative electrode prepared in the same manner as the item (said 8.) of preparation of non-aqueous battery was applied to both sides of copper foil in a thickness of 0.02 mm, dried and  
5 rolled to obtain a negative electrode plate having a thickness of 0.10mm, width of 55mm and length of 90 mm.

A solid electrolyte,  $(\text{PEO})_8 \cdot \text{LiClO}_4$ , was prepared by dissolving polyethyleneoxide (molecular weight 600,000) and  $\text{LiClO}_4$  in acetonitrile, followed by  
10 casting the solution on a PTFE membrane ("TEFLON" product of DUPONT) under argon atmosphere in glovebox, and then distillating the solvent by allowing it to stand at 25 °C in glovebox.

A film-type lithium secondary battery was  
15 prepared by using carbonized pitch-coated graphite or graphitized pitch-coated graphite as negative electrode body,  $\text{LiCoO}_2$  as solid electrolyte and positive electrode body and  $(\text{PEO})_8 \cdot \text{LiClO}_4$  as solid electrolyte.

Electrical discharge properties of  
20 lithium secondary battery thus prepared were determined. The determination was carried out under constant-current charge and discharge of  $1\text{mA}/\text{cm}^2$ . Discharge capacity was regarded as capacity until battery voltage was decreased to 1.2V.

25 Example 1

50g of massive artificial graphite (center particle diameter D50 =  $7.5\mu\text{m}$ ; particle size distribution 0.1-150 $\mu\text{m}$ ;  $d_{002}=0.336\text{nm}$ ;  $L_c=100\text{nm}$ ;  $L_a=97\text{nm}$ ; specific surface area =  $10.8\text{m}^2/\text{g}$ ; R value = 0.26; true specific gravity =  $2.25\text{g}/\text{cm}^3$ ) and 100g of coal tar pitch (softening point  $80^\circ\text{C}$ ; quinoline insoluble matter = trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 500ml reaction flask. The mixture was stirred for 2 hours at  $200^\circ\text{C}$  under normal pressure to give crude pitch-coated graphite. Toluene (1 part) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at  $80^\circ\text{C}$  for 1 hour for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as  $7.7\mu\text{m}$ . Since center particle diameter D50 of graphite as core material was  $7.5\mu\text{m}$ , a thickness of pitch layer is  $0.1\mu\text{m}$ .

The quinoline soluble matter, specific surface area and true specific gravity of the resulting purified pitch-coated graphite are shown in table 1. Since quinoline soluble matter was 9.6%, a covering ratio of the purified pitch-coated graphite is 0.096.

The purified pitch-coated graphite was calcined at  $1,000^\circ\text{C}$  for 1 hour under nitrogen atmosphere (heating

rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite are shown in table 1. The results of determination of particle size distribution of the purified pitch-coated graphite indicated that the coated graphite has a distribution within 0.1-150  $\mu$ m. The results of X-ray diffractometry thereof were similar to those of core material.

Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicate that artificial graphite as core material was coated with carbonized pitch forming a coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

Furthermore, a negative electrode was produced using a negative electrode which was produced by using



the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 3.

Example 2

5           The purified pitch-coated graphite obtained according to example 1 was calcined at 1,000°C for 1 hour under vacuum of 10 torr (heating rate 25°C/hr) for vacuum carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of  
10 particles having a diameter of 1 $\mu$ m or less of the resulting vacuum carbonized pitch-coated graphite are shown in table 1. The results of determination of particle size distribution of the vacuum carbonized pitch-coated graphite indicated that the coated graphite  
15 had a distribution within 0.1-150  $\mu$ m as core material. The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between core material and vacuum carbonized pitch-coated graphite indicated that carbonized pitch forming a  
20 coating layer had lower crystallinity than core material. The results of SEM observation indicated that artificial graphite as core material are coated with vacuum carbonized pitch forming a coating layer and that edge parts thereof were rounded.

25           A non-aqueous secondary battery was produced

using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the vacuum carbonized pitch-coated graphite. The results of  
5 determination of charge and discharge properties thereof are shown in table 2.

### Example 3

The purified pitch-coated graphite obtained according to example 1 was calcined at 2,800°C for 1 hour  
10 under nitrogen atmosphere for graphitization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1µm or less of the resulting graphitized pitch-coated graphite are shown in table 1. The results  
15 of determination of particle size distribution of the graphitized pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150 µm as core material. The results of X-ray diffractometry thereof were similar to those of core material.  
20 Furthermore, comparison of R values between core material and graphitized pitch-coated graphite indicated that graphitized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicated that artificial graphite as core  
25 material was coated with graphitized pitch forming a

coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, a mixed solvent of ethylene carbonate, diethyl carbonate and methyl-  
5 propionate (3:3:4) in which 1 mol $\text{dm}^{-3}$  of  $\text{LiClO}_4$  was dissolved and a negative electrode which was produced by using the graphatized pitch-coated graphite.

The amount of generated gas of the graphatized pitch-coated graphite in the electrolytic solution was  
10 determined. The results of determination of charge and discharge properties and the amount of generated gas are shown in table 2.

#### Example 4

The purified pitch-coated graphite obtained  
15 according to example 1 was calcined at 1,000°C in a lead furnace capable of elevating temperature very slowly (reducing atmosphere, heating rate of up to 5°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of  
20 particles having a diameter of 1 $\mu\text{m}$  or less of the resulting carbonized pitch-coated graphite are shown in table 1. The results of determination of particle size distribution of the carbonized pitch-coated graphite indicated that the coated graphite had a distribution  
25 within 0.1-150  $\mu\text{m}$  as core material. The results of X-ray

diffractionmetry thereof were similar to those of core material. Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch forming a coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

#### Example 5

The purified pitch-coated graphite obtained according to example 1 was calcined at 1,300°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1µm or less of the carbonized pitch-coated graphite are shown in table 1. The results of determination of particle size distribution of the carbonized pitch-coated graphite

indicated that the coated graphite had a distribution within 0.1-150  $\mu\text{m}$  as core material. The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between  
5 core material and carbonized pitch-coated graphite indicated that carbonized pitch forming a coating layer has lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch forming a  
10 coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1  $\text{mol dm}^{-3}$  of  $\text{LiClO}_4$  was dissolved and a negative electrode which was produced by using the carbonized  
15 pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

#### Example 6

The purified pitch-coated graphite obtained  
20 according to example 1 was treated for oxidation at 300°C for 8 hours under air atmosphere in a chamber with constant temperature and relative humidity. The covering ratio, specific surface area and true specific gravity of the resulting oxidized and purified pitch-coated graphite  
25 are shown in table 1. The oxidized and purified pitch-

coated graphite was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite are shown in table 1. The results of determination of particle size distribution of the carbonized pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m as core material. The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch forming a coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 mol $\text{dm}^{-3}$  of  $\text{LiClO}_4$  was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

Example 7

50g of massive artifitial graphite (center particle diameter D50 = 7.5 $\mu$ m; particle size distribution 0.1-150 $\mu$ m; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>) and 100g of coal tar pitch (softening point 80°C; quinoline insoluble matter = trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 500ml reaction flask. The mixture was stirred for 2 hours at 200°C to give crude pitch-coated graphite.

Toluene (1 part) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 20°C for 1 hour for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as 7.9 $\mu$ m. Since center particle diameter D50 of graphite as core material was 7.5 $\mu$ m, a thickness of pitch layer is 0.2 $\mu$ m.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline soluble matter thereof was 20.4%, a covering ratio of the purified pitch-coated graphite is 0.204.

The purified pitch-coated graphite thus

obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less with respect to the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m. The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch forming a coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.



Example 8

The purified pitch-coated graphite obtained according to example 7 was calcined at 2,800°C for 1 hour under nitrogen atmosphere for graphitization. The

5 specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the resulting graphitized pitch-coated graphite are shown in table 1. The results

of determination of particle size distribution of the

10 graphitized pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m as core material. The results of X-ray diffractometry

thereof were similar to those of core material. Furthermore, comparison of R values between core material

15 and graphitized pitch-coated graphite indicated that graphitized pitch forming a coating layer had lower

crystallinity than core material. The results of SEM observation indicated that artificial graphite as core material was coated with graphitized pitch forming a

20 coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, a mixed solvent of ethylene carbonate, diethyl carbonate and methyl-

propionate (3:3:4) in which 1 mol $\text{dm}^{-3}$  of  $\text{LiClO}_4$  was

25 dissolved and a negative electrode which was produced by

using the graphatized pitch-coated graphite. The amount of generated gas of the graphatized pitch-coated graphite in the electrolytic solution was determined. The results of determination of charge and discharge properties and  
5 the amount of generated gas are shown in table 2.

Example 9

50g of massive artifitial graphite (center particle diameter D50 = 7.5 $\mu$ m; particle size distribution 0.1-150 $\mu$ m; d002=0.336nm; Lc=100nm; La=97nm; specific  
10 surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>) and 100g of coal tar pitch (softening point 80°C; quinoline insoluble matter = trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 500ml reaction  
15 flask. The mixture was stirred for 2 hours at 200°C under reduced pressure (evacuated with a vacuum pump; reduced pressure = 50 torr) to give crude pitch-coated graphite.

Toluene (1 part) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture  
20 was stirred at 80°C for 1 hour for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as 7.7 $\mu$ m. Since center particle  
25 diameter D50 of graphite as core material was 7.5 $\mu$ m, a

thickness of pitch layer is 0.1 $\mu$ m.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline  
5 soluble matter thereof was 10.4%, a covering ratio of the purified pitch-coated graphite is 0.104.

The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for  
10 carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size  
15 distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m as core material. The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between  
20 core material and carbonized pitch-coated graphite indicated that carbonized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicated that artificial graphite as core material was coated with carbonized pitch forming a  
25 coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized  
5 pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

Example 10

50g of massive artificial graphite (center  
10 particle diameter D50 = 7.5μm; particle size distribution 0.1-150μm; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>2</sup>) and 100g of coal tar pitch (softening point 80°C; quinoline insoluble matter =  
15 trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 500ml reaction flask. The mixture was stirred for 2 hours at 200°C to give crude pitch-coated graphite.

Tar middle oil (1 part) was added to the crude  
20 pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 20°C for 1 hour for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as 7.6μm. Since  
25 center particle diameter D50 of graphite as core material

is 7.5 $\mu$ m, a thickness of pitch layer is 0.05 $\mu$ m.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline  
5 soluble matter thereof was 8.8%, a covering ratio of the purified pitch-coated graphite is 0.088.

The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for  
10 carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size  
15 distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m as core material. The results of X-ray diffractometry thereof are similar to those of core material. Furthermore, comparison of R values between  
20 core material and graphitized pitch-coated graphite indicated that graphitized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicated that artificial graphite as core material was coated with graphitized pitch forming a  
25 coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

Example 11

50g of massive artificial graphite (center particle diameter D50 = 7.5μm; particle size distribution 0.1-150μm; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>) and 200g of coal tar pitch (softening point 80°C; quinoline insoluble matter = trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 1,000ml reaction flask. The mixture was stirred for 2 hours at 200°C to give crude pitch-coated graphite.

Toluene (1 part) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 80°C for 1 hour for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as 7.9μm. Since center particle diameter D50 of graphite as core material is 7.5μm,

thickness of pitch layer is 0.2 $\mu$ m.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline  
5 soluble matter thereof was 17.3%, a covering ratio of the purified pitch-coated graphite is 0.173.

The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for  
10 carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size  
15 distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m as core material. The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between  
20 core material and graphitized pitch-coated graphite indicated that carbonized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicated that artificial graphite as core material was coated with carbonized pitch forming a  
25 coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

Example 12

50g of massive artificial graphite (center particle diameter D50 = 7.5μm; particle size distribution 0.1-150μm; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>) and 100g of coal tar pitch (softening point 80°C; quinoline insoluble matter = 3.9%; toluene insoluble matter = 34%) whose primary QI was not removed were added to a 500ml reaction flask. The mixture was stirred for 2 hours at 200°C under normal pressure to give crude pitch-coated graphite.

Toluene (1 part) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 80°C for 1 hour for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as 7.9μm. Since center particle diameter D50 of graphite as core material was 7.5μm,



thickness of pitch layer is 0.2 $\mu$ m.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline  
5 soluble matter thereof was 7.5%, a covering ratio of the purified pitch-coated graphite is 0.075.

The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for  
10 carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less with respect to the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of  
15 particle size distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m as core material. The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R  
20 values between core material and carbonized pitch-coated graphite indicated that carbonized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicated that artificial graphite as core material was coated with carbonized  
25 pitch forming a coating layer and that edge parts thereof

were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

#### Example 13

10                50g of massive artifitial graphite (center particle diameter D50 = 7.5μm; particle size distribution 0.1-150μm; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>2</sup>) and 100g of coal tar pitch  
15 (softening point 10°C; quinoline insoluble matter = trace; toluene insoluble matter = 8%) whose primary QI was removed previously were added to a 500ml reaction flask. The mixture was stirred for 2 hours at 200°C under normal pressure to give crude pitch-coated  
20 graphite.

Toluene (1 part) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 80°C for 1 hour for washing treatment and filtered to give purified pitch-coated graphite. Center  
25 particle diameter D50 of the purified pitch-coated

graphite was determined as 7.6 $\mu$ m. Since center particle diameter D50 of graphite as core material is 7.5 $\mu$ m, a thickness of pitch layer is 0.05 $\mu$ m.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline soluble matter thereof was 7.8%, a covering ratio of the purified pitch-coated graphite is 0.078.

The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m as core material. The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as

core material was coated with carbonized pitch forming a coating layer and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate  
5 in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

10 Furthermore, a negative electrode which was produced by using the carbonized pitch-coated graphite, and then a solid electrolyte lithium secondary battery was produced. The results of determination of charge and discharge properties thereof are shown in table 3.

15 Example 14

50g of graphitized spheric mesocarbon microbeads ("MCMB-6-28" product of Osaka Gas Co., Ltd., center particle diameter D50 = 6.0μm; particle size distribution 0.1-50μm; d002=0.336nm; Lc=50nm; La=90nm;  
20 specific surface area = 3.0m<sup>2</sup>/g; R value = 0.42; true specific gravity = 2.20g/cm<sup>3</sup>) and 100g of coal tar pitch (softening point 80°C; quinoline insoluble matter = trace; toluene insoluble matter = 30%) whose primary QI  
25 flask. The mixture was stirred for 2 hours at 200°C

under normal pressure to give crude pitch-coated mesocarbon microbeads.

Toluene (1 part) was added to the crude pitch-coated mesocarbon microbeads thus obtained (1 part), and  
5 the mixture was stirred at 80°C for 1 hour for washing treatment and filtered to give purified pitch-coated mesocarbon microbeads. Center particle diameter D50 of the purified pitch-coated mesocarbon microbeads was determined as 6.2 $\mu$ m. Since center particle diameter D50  
10 of graphite as core material was 6.0 $\mu$ m, a thickness of pitch layer is 0.1 $\mu$ m.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated mesocarbon microbeads obtained are shown in table 1.  
15 Since quinoline soluble matter thereof was 9.8%, a covering ratio thereof is 0.098.

The purified pitch-coated graphitized mesocarbon microbeads thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating  
20 rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the purified pitch-coated graphitized mesocarbon microbeads are shown in table 1. The results of  
25 determination of particle size distribution of the

purified pitch-coated graphitized mesocarbon microbeads indicated that the mesocarbon microbeads had a distribution within 0.1-50  $\mu\text{m}$  as core material. Furthermore, comparison of R values between core material  
5 and carbonized pitch-coated graphitized mesocarbon microbeads indicated that carbonized pitch forming a coating layer had lower crystallinity than core material.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate  
10 in which 1  $\text{mol dm}^{-3}$  of  $\text{LiClO}_4$  was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphitized mesocarbon microbeads. The results of determination of charge and discharge properties thereof are shown in table 2.

15 Example 15

50g of massive artifitial graphite (center particle diameter D50 = 16.2 $\mu\text{m}$ ; particle size distribution 0.1-120 $\mu\text{m}$ ; d002=0.337nm; Lc=100nm; La=71nm; specific surface area = 14.4 $\text{m}^2/\text{g}$ ; R value = 0.31; true  
20 specific gravity = 1.96 $\text{g/cm}^3$ ) and 100g of coal tar pitch (softening point 80°C; quinoline insoluble matter = trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 1,000ml reaction flask. The mixture was stirred for 5 hours at 250°C  
25 under normal pressure to give crude pitch-coated

graphite.

Toluene (3 parts) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 50°C for 5 hour for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as 16.6 $\mu$ m. Since center particle diameter D50 of graphite as core material is 16.2 $\mu$ m, a thickness of pitch layer is 0.2 $\mu$ m.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline soluble matter thereof was 11.3%, a covering ratio of the purified pitch-coated graphite is 0.113.

The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less with respect to the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-120  $\mu$ m as core material. The

results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch forming a coating layer had lower crystallinity than core material. The results of SEM observation indicated that artificial graphite as core material was coated with carbonized pitch, i.e., coat-forming carbon materials and that edge parts thereof were rounded.

10           A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 mol dm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

#### Example 16

50g of massive artificial graphite (center particle diameter D50 = 16.2μm; particle size distribution 1-80μm; d002=0.338nm; Lc=83nm; La=63nm; specific surface area = 6.8m<sup>2</sup>/g; R value = 0.38; true specific gravity = 2.02g/cm<sup>3</sup>) and 100g of coal tar pitch (softening point 80°C; quinoline insoluble matter = trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 1,000ml reaction



flask. The mixture was stirred for 5 hours at 250°C under normal pressure to give crude pitch-coated graphite.

Toluene (3 parts) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 50°C for 5 hour for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as 12.0µm. Since center particle diameter D50 of graphite as core material was 11.6µm, a thickness of pitch layer is 0.2µm.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline soluble matter thereof was 12.3%, a covering ratio of the purified pitch-coated graphite is 0.123.

The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1µm or less with respect to the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size distribution of the purified pitch-coated

graphite indicated that the coated graphite had a distribution within 1-80  $\mu\text{m}$ . The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between  
5 core material and carbonized pitch-coated graphite indicated that carbonized pitch, i.e., coat-forming carbon materials had lower crystallinity than core material. The results of SEM observation indicated that artificial graphite as core material was coated with  
10 carbonized pitch, i.e., coat-forming carbon materials and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1  $\text{mol dm}^{-3}$  of  $\text{LiClO}_4$  was dissolved and a negative  
15 electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

#### Example 17

20 50g of scaly artificial graphite (center particle diameter D50 = 18.9 $\mu\text{m}$ ; particle size distribution 0.1-150 $\mu\text{m}$ ; d002=0.340nm; Lc=42nm; La=50nm; specific surface area = 9.2 $\text{m}^2/\text{g}$ ; R value = 0.49; true specific gravity = 1.82 $\text{g/cm}^3$ ) and 100g of coal tar pitch  
25 (softening point 80°C; quinoline insoluble matter =

trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 1,000ml reaction flask. The mixture was stirred for 5 hours at 250°C under normal pressure to give crude pitch-coated

5 graphite.

Toluene (3 parts) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 50°C for 5 hour for washing treatment and filtered to give purified pitch-coated graphite. Center  
10 particle diameter D50 of the purified pitch-coated graphite was determined as 19.3 $\mu$ m. Since center particle diameter D50 of graphite as core material was 18.9 $\mu$ m, a thickness of pitch layer is 0.2 $\mu$ m.

The covering ratio, specific surface area and  
15 true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline soluble matter thereof was 10.6%, a covering ratio of the purified pitch-coated graphite is 0.106.

The purified pitch-coated graphite thus  
20 obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the  
25 carbonized pitch-coated graphite obtained are shown in

table 1. The results of determination of particle size distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu\text{m}$ . The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch, i.e., coat-forming carbon materials had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch, i.e., coat-forming carbon materials and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1  $\text{mol dm}^{-3}$  of  $\text{LiClO}_4$  was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

#### Example 18

50g of whisker artifitial graphite (center particle diameter D50 = 23.8 $\mu\text{m}$ ; particle size distribution 0.1-150 $\mu\text{m}$ ;  $d_{002}$ =0.347nm;  $L_c$ =25nm;  $L_a$ =15nm; specific surface area = 13.5 $\text{m}^2/\text{g}$ ; R value = 0.68; true

specific gravity =  $1.60\text{g/cm}^3$ ), and 100g of coal tar pitch (softening point  $80^\circ\text{C}$ ; quinoline insoluble matter = trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 1,000ml reaction flask. The mixture was stirred for 5 hours at  $250^\circ\text{C}$  under normal pressure to give crude pitch-coated graphite.

Toluene (3 parts) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at  $50^\circ\text{C}$  for 5 hours for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as  $24.2\mu\text{m}$ . Since center particle diameter D50 of graphite as core material was  $23.8\mu\text{m}$ , a thickness of pitch layer is  $0.2\mu\text{m}$ .

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline soluble matter thereof was 13.1%, a covering ratio of the purified pitch-coated graphite is 0.131.

The purified pitch-coated graphite thus obtained was calcined at  $1,000^\circ\text{C}$  for 1 hour under nitrogen atmosphere (heating rate  $25^\circ\text{C/hr}$ ) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of

particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size distribution of the purified pitch-coated graphite

5 indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m. The results of X-ray diffractometry thereof were similar to those of core material.

Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that

10 carbonized pitch, i.e., coat-forming carbon materials had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch, i.e., coat-forming carbon materials and that edge parts thereof  
15 were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized  
20 pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

#### Example 19

50g of massive artifitial graphite (center  
25 particle diameter D50 = 7.5 $\mu$ m; particle size distribution

0.1-150 $\mu$ m; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>) and 100g of coal tar pitch

(softening point 80°C; quinoline insoluble matter =

5 trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 500ml reaction flask. The mixture was stirred for 1 hour at 300°C under normal pressure to give crude pitch-coated graphite.

Quinoline (0.1 part) was added to the crude  
10 pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 150°C for 10 hours for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified  
15 pitch-coated graphite was determined as 8.1 $\mu$ m. Since center particle diameter D50 of graphite as core material was 7.5 $\mu$ m, thickness of pitch layer is 0.3 $\mu$ m.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline  
20 soluble matter thereof was 29.0%, a covering ratio of the purified pitch-coated graphite is 0.290.

The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 100°C/hr) for  
25 carbonization. The specific surface area, true specific

gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m. The results of X-ray diffractometry thereof were similar to those of core material.

Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch, i.e., coat-forming carbon materials had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch, i.e., coat-forming carbon materials and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 mol $\text{dm}^{-3}$  of  $\text{LiClO}_4$  was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

#### Example 20

25g of massive artifitial graphite (center



particle diameter D50 = 7.5 $\mu$ m; particle size distribution 0.1-150 $\mu$ m; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>) and 50g of coal tar pitch (softening point 80°C; quinoline insoluble matter = trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 1,000ml reaction flask. The mixture was stirred for 3 hours at 30°C under normal pressure to give crude pitch-coated graphite.

10                   Acetone (10 parts) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 30°C for 5 hours for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified  
15 pitch-coated graphite was determined as 7.8 $\mu$ m. Since center particle diameter D50 of graphite as core material was 7.5 $\mu$ m, a thickness of pitch layer is 0.15 $\mu$ m.

                  The covering ratio, specific surface area and true specific gravity of the purified pitch-coated  
20 graphite obtained are shown in table 1. Since quinoline soluble matter thereof was 15.0%, a covering ratio of the purified pitch-coated graphite is 0.150.

                  The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under  
25 nitrogen atmosphere (heating rate 25°C/hr) for

carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of to the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m. The results of X-ray diffractometry thereof were similar to those of core material.

Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch, i.e., coat-forming carbon materials had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch, i.e., coat-forming carbon materials and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

Example 21

50g of massive artificial graphite (center particle diameter D50 = 7.5 $\mu$ m; particle size distribution 0.1-150 $\mu$ m; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>) and 50g of coal tar pitch (softening point 10°C; quinoline insoluble matter = trace; toluene insoluble matter = 8%) whose primary QI was removed previously were added to a 500ml reaction flask. The mixture was stirred for 3 hours at 250°C under normal pressure to give crude pitch-coated graphite.

Tar middle oil (10 parts) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 200°C for 1 hour for washing treatment and filtered to give purified pitch-coated graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as 7.5 $\mu$ m.

The covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline soluble matter thereof was 2.0%, a covering ratio of the purified pitch-coated graphite is 0.020.

The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for carbonization. The specific surface area, true specific

gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m. The results of X-ray diffractometry thereof were similar to those of core material.

Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch, i.e., coat-forming carbon materials had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch, i.e., coat-forming carbon materials and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

#### Example 22

25                    50g of massive artifitial graphite (center

particle diameter D50 = 7.5 $\mu$ m; particle size distribution 0.1-150 $\mu$ m; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>) and 100g of coal tar pitch

5 (softening point 80°C; quinoline insoluble matter = trace; toluene insoluble matter = 8%) whose primary QI was removed previously were added to a 1,000ml reaction flask. The mixture was stirred for 3 hours at 250°C under normal pressure to give crude pitch-coated  
10 graphite.

Toluene (4 parts) was added to the crude pitch-coated graphite thus obtained (1 part), and the mixture was stirred at 80°C for 1 hour for washing treatment and filtered to give purified pitch-coated  
15 graphite. Center particle diameter D50 of the purified pitch-coated graphite was determined as 7.6 $\mu$ m. Since center particle diameter D50 of graphite as core material was 7.5 $\mu$ m, a thickness of pitch layer is 0.05 $\mu$ m.

The covering ratio, specific surface area and  
20 true specific gravity of the purified pitch-coated graphite obtained are shown in table 1. Since quinoline soluble matter thereof was 8.2%, a covering ratio of the purified pitch-coated graphite is 0.082.

The purified pitch-coated graphite thus  
25 obtained was calcined at 700°C for 1 hour under nitrogen

atmosphere (heating rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite obtained are shown in table 1. The results of determination of particle size distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m. The results of X-ray diffractometry thereof were similar to those of core material. Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch, i.e., coat-forming carbon materials had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch, i.e., coat-forming carbon materials and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

Example 23

The purified pitch-coated graphite obtained according to example 22 was calcined at 1,500°C for 2 hour (heating rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the resulting carbonized pitch-coated graphite are shown in table 1. The results of determination of particle size distribution of the carbonized pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m as core material. The results of X-ray diffractometry thereof were similar to those of core material.

Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch, i.e., coat-forming carbon materials had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as core material was coated with carbonized pitch, i.e., coat-forming carbon materials and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of

charge and discharge properties thereof are shown in table 2.

Example 24

50g of massive artificial graphite (center  
5 particle diameter D50 = 7.5 $\mu$ m; particle size distribution  
0.1-150 $\mu$ m; d002=0.336nm; Lc=100nm; La=97nm; specific  
surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific  
gravity = 2.25g/cm<sup>3</sup>) and 100g of coal tar pitch  
(softening point 10°C; quinoline insoluble matter = 2.9%;  
10 toluene insoluble matter = 7.8%) whose primary QI was  
adjusted previously were added to a 1,000ml reaction  
flask. The mixture was stirred for 2 hours at 200°C  
under normal pressure to give crude pitch-coated  
graphite.

15 Toluene (4 parts) was added to the crude  
pitch-coated graphite thus obtained (1 part), and the  
mixture was stirred at 80°C for 1 hour for washing  
treatment and filtered to give purified pitch-coated  
graphite. Center particle diameter D50 of the purified  
20 pitch-coated graphite was determined as 7.6 $\mu$ m. Since  
center particle diameter D50 of graphite as core material  
was 7.5 $\mu$ m, a thickness of pitch layer is 0.05 $\mu$ m.

The covering ratio, specific surface area and  
true specific gravity of the purified pitch-coated  
25 graphite obtained are shown in table 1. Since quinoline



soluble matter thereof was 8.7%, a covering ratio of the purified pitch-coated graphite is 0.087.

The purified pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under  
5 nitrogen atmosphere (heating rate 25°C/hr) for carbonization. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of 1 $\mu$ m or less of the carbonized pitch-coated graphite obtained are shown in  
10 table 1. The results of determination of particle size distribution of the purified pitch-coated graphite indicated that the coated graphite had a distribution within 0.1-150  $\mu$ m. The results of X-ray diffractometry thereof were similar to those of core material.  
15 Furthermore, comparison of R values between core material and carbonized pitch-coated graphite indicated that carbonized pitch, i.e., coat-forming carbon materials had lower crystallinity than core material. The results of SEM observation indicated that artifitial graphite as  
20 core material was coated with carbonized pitch, i.e., coat-forming carbon materials and that edge parts thereof were rounded.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate  
25 in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative

electrode which was produced by using the carbonized pitch-coated graphite. The results of determination of charge and discharge properties thereof are shown in table 2.

5 Comparative example 1

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by using massive artificial  
10 graphite (center particle diameter D50 = 7.5μm; particle size distribution 0.1-150μm; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>).

However, the battery can hardly be charged and  
15 discharged due to decomposition of the electrolytic solution.

A covering ratio, specific surface area and true specific gravity of the purified pitch-coated graphite obtained are shown in table 1.

20 Comparative example 2

A non-aqueous secondary battery was produced using, as an electrolytic solution, a mixed solvent of ethylene carbonate, diethyl carbonate and methylpropionate (3:3:4) in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was  
25 dissolved and a negative electrode which was produced by

using massive artificial graphite (center particle diameter D50 = 7.5 $\mu$ m; particle size distribution 0.1-150 $\mu$ m; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>). The amount of generated gas of the graphite in the electrolytic solution was determined. The results of determination of charge and discharge properties and the amount of generated gas are shown in table 2.

Comparative example 3

10                   A negative electrode was produced by using massive artificial graphite (center particle diameter D50 = 7.5 $\mu$ m; particle size distribution 0.1-150 $\mu$ m; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>). A solid electrolyte lithium secondary battery was then produced using the negative electrode. The results of determination of charge and discharge properties thereof are shown in table 3.

Comparative example 4

20                   A non-aqueous secondary battery was produced using, as an electrolytic solution, a mixed solvent of ethylene carbonate, diethyl carbonate and methylpropionate (3:3:4) in which 1 moldm<sup>-3</sup> of LiClO<sub>4</sub> was dissolved and a negative electrode which was produced by 25 using graphitized spheric mesocarbon microbeads ("MCMB-6-

28" product of Osaka Gas Co., Ltd., center particle diameter D50 = 6.0 $\mu$ m; particle size distribution 0.1-50 $\mu$ m; d002=0.336nm; Lc=50nm; La=90nm; specific surface area = 3.0m<sup>2</sup>/g; R value = 0.42; true specific gravity = 2.20g/cm<sup>3</sup>). The results of determination of charge and discharge properties thereof are shown in table 2.

Comparative example 5

50g of massive artifitial graphite (center particle diameter D50 = 7.5 $\mu$ m; particle size distribution 0.1-150 $\mu$ m; d002=0.336nm; Lc=100nm; La=97nm; specific surface area = 10.8m<sup>2</sup>/g; R value = 0.26; true specific gravity = 2.25g/cm<sup>3</sup>) and 100g of coal tar pitch (softening point 80°C; quinoline insoluble matter = trace; toluene insoluble matter = 30%) whose primary QI was removed previously were added to a 1,000ml reaction flask. The mixture was stirred for 2 hours at 200°C under normal pressure to give crude pitch-coated graphite.

The crude pitch-coated graphite thus obtained was calcined at 1,000°C for 1 hour under nitrogen atmosphere (heating rate 25°C/hr) for carbonization without washing the crude pitch-coated graphite with organic solvents. After calcination, the artifitial graphite powder was taken out as lump. The lump of carbon material was grinded with a coffee mill to obtain

carbon material powders. The specific surface area, true specific gravity, R value and volume-based integrated value of particles having a diameter of  $1\mu\text{m}$  or less of the obtained carbon materials are shown in table 1. The results indicate small R value thereof. The SEM observation demonstrates that the carbon materials has an angular shape in the carbon materials produced according to the method of the invention. The angular shape seems to result from exposure of graphite face caused by grinding.

A non-aqueous secondary battery was produced using, as an electrolytic solution, propylene carbonate in which  $1\text{ mol dm}^{-3}$  of  $\text{LiClO}_4$  was dissolved and a negative electrode which was produced by using the carbon materials. The results of determination of charge and discharge properties thereof are shown in table 2.



Table 2

		Discharge capacity (mAh/g)	Efficiency of charge and discharge(%)	Generated gas (ml/g)
5	Example 1	355	83.4	-
	Example 2	370	86.0	-
	Example 3	343	86.2	2.2
	Example 4	346	85.9	-
	Example 5	349	86.1	-
10	Example 6	359	85.3	-
	Example 7	342	85.5	-
	Example 8	334	90.5	1.7
	Example 9	348	87.8	-
	Example 10	351	84.2	-
15	Example 11	344	89.5	-
	Example 12	339	82.4	-
	Example 13	342	90.1	-
	Example 14	334	90.5	-
	Example 15	330	82.5	-
20	Example 16	316	82.1	-
	Example 17	310	87.6	-
	Example 18	303	88.7	-
	Example 19	331	88.6	-
	Example 20	340	82.7	-
25	Example 21	357	80.6	-
	Example 22	321	83.0	-
	Example 23	359	80.4	-
	Example 24	350	82.8	-
30	Comp.Ex.1	Determination is impossible due to decomposition of solvent		
	Comp.Ex.2	224	51.0	15.0
	Comp.Ex.4	303	90.2	-
	Comp.Ex.5	302	68.1	-

Table 3		
	Discharge capacity (mAh/g)	Efficiency of Charge and Discharge(%)
Ex. 1	350	83.1
5    Comp.ex. 3	210	49.0

As shown in table 1, coating a graphite surface by pitch or tar can reduce specific surface area thereof. The specific surface area is further reduced by calcination of the coated graphite.

10            As shown in table 2, coating a graphite surface with pitch or tar greatly improves discharge capacity and efficiency of charge and discharge of non-aqueous lithium secondary battery. Coating a graphite surface by pitch inhibits a reactivity of the graphite to the electrolytic  
15    solution and reduces the amount of generated gas.

As shown in table 3, discharge capacity and efficiency of charge and discharge of battery may be greatly improved by coating a graphite surface with pitch or tar with respect to solid electrolyte lithium  
20    secondary battery.